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(54) **Thermoplastic compositions comprising starch and other components from natural origin**

(57) Biodegradable thermoplastic compositions comprising a starch component, a cellulose ester or ether, a plasticizer for the starchy phase and of the cellulose and derivatives, and a compatibilizer agent selected from polymers compatible with the cellulose and or starchy component, grafted with aliphatic or polyhydroxylated chains: copolymers obtained from hydroxy

acids and/or diamines with 2 -24C and aliphatic or aromatic diisocyanates; copolymers obtained from aliphatic polyesters, polyureas and polyalkylene glycols and aliphatic or aromatic diisocyanates; copolymers obtained from polymers compatible with cellulose ester or ethers and/or the starchy component by grafting starch soluble polyols; polymer capable of complexing starch; starch compatible polyols.

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Description

The present invention relates to biodegradable thermoplastic composition suitable, in particular for preparing injection moulded articles free from surface defects, comprising a starchy component and a cellulose ester or ether.

Biodegradable composition obtained starting from starch and a thermoplastic polymer are well known in the art and available from the market and are disclosed, e. g., in European patent applications EPA 32 802, 327 505, 400 532, 404 723, 404 727, 404 728, and in W090/0671, W071/02025, USP5 095 054.

Typically, such compositions can be obtained by blending starch and a synthetic thermoplastic polymer, under extrusion cooking conditions, i.e. in the presence of limited amounts of water (generally 0.5-40% by weight based on starch-water system) or of a plasticiser, by operating under temperature and pressure conditions sufficient to destroy the starch crystallinity and to obtain a thermoplastic molten mass (destructured starch).

From European patent application EPA 575 349, biodegradable compositions are known which comprise a starch component and a cellulose ester.

The injection moulded articles obtained starting from said compositions are affected from the drawback of displaying unpleasant surface scale due to the poor compatibility between starch and cellulose esters. European patent application EPA 542 155 discloses compositions based on starch and cellulose esters added with a compatibilizer agent (epoxidized soy bean oil and acetylated starch) in order to confer improved mechanical properties to the moulded articles. The moulded articles from the above compositions undergo considerable delamination phenomena due to the insufficient compatibilization between starch and the cellulose ester.

We have found now that it is possible to improve the mutual compatibility of starch or starch esters or ethers and cellulose esters or ethers and to obtain moulded articles free from scales unevenness, by using selected classes of compatibilizing agents.

Beside endowing the resulting compositions with better homogeneity, the use of the compatibilizing agents of the invention improves the biodegradability characteristics of the compositions.

The compositions according to the present invention comprise:

- starch or a starch ester or ether with a substitution degree from about 1.2 to 2.5;
- a cellulose ester or ether with a substitution degree from about 1.2 to 2.5;
- a plasticizer for the starchy phase and a plasticizer for the cellulose derivatives phase or a plasticizer for both phases;
- a compatibilizing agent selected from the following classes:

(A) polymers compatible with cellulose esters or ethers and/or starch or starch esters and ethers, grafted with aliphatic or polyhydroxylated chains containing from 4 to 40 carbon atoms;

(B) copolymers obtained from hydroxy acids and/or diamines with 2-24 carbon atoms and aliphatic or aromatic diisocyanates or epoxy compounds and anhydrides; copolymers obtained from aliphatic polyesters, polyamides or polyureas and aliphatic or aromatic diisocyanates; copolymers obtained from aliphatic or aromatic diisocyanates and polyalkylene glycols;

(C) copolymers obtained from polymers compatible with cellulose esters or ethers and/or starch or starch esters or ethers, by grafting starch soluble polyols or structures capable of complexing starch.

(D) polymers capable of complexing starch such as ethylene - vinyl alcohol or ethylene acrylic acid copolymers, aliphatic polyesters or polyamides.

(E) starch compatible polyols selected from the monomers and the low molecular weight polyols (MW lower than 10.000) such as glycerol, sorbitol, erythritol, polyglycerol, destrines, polyvinylalcohol, polyaspartates, and the above polyols grafted with alkyl oxides or polyalkyl oxides. The compatibilizer agents indicated under (A) are obtained by grafting aliphatic chains with 4-40 carbon atoms optionally containing up to three unsaturations and or heteroatoms or still other functional groups, to polymers compatible with cellulose esters or cellulose ethers. Preferably, the chains derive from animal or vegetable fats, such as oleic, lauric, myristic, palmitic, stearic, euric, linoleic, ricinoleic acids or phospholipids with terminal end groups which allow the chains to be grafted to the polymers compatible with cellulose esters or ethers.

The terminal group can be carboxy, ester or salt groups; the chains can also be modified in order to obtain terminal groups such as alcohol, aldehyde, amine, amide, acid chloride, isocyanate, mercaptan epoxy and anhydride groups. The polymers to which the above said lipidic chains are grafted can display different degrees of affinity with cellulose derivatives and starch esters or ether: some of them can even be miscible with said cellulose derivatives and starch ester or ethers; others, with a lower compatibility degree, can anyway result to be interesting because they can be easily transformed into compatible derivatives.

Such polymers can be of either natural or synthetic origin. Furthermore, they can be used as such, or modified or

depolymerized to trimer level by hydrolysis, saponification, cracking or by means of enzymatic reactions.
Examples of the above polymers are:

- (a) cellulose esters with various DS (Degree of Substitution);
- (b) cellulose ethers with various DS;
- (c) cellulose ethers/esters with various DS values;
- (d) starch ester with various DS values, as acetates;
- (e) starch ethers with various DS values, such as the reaction products of starch with ethylene or propylene glycols;
- (f) starch ethers/esters with various DS values;
- (g) partially hydrolysed polyvinyl acetate;
- (m) aliphatic polyesters and copolyesters, optionally also grafted with those products as listed under (a) - (i) above. In this case, polymers are preferred which are obtained by grafting low molecular weight (350-1000) polycaprolactone (PCL) to polyvinyl alcohol copolymer or, also, by grafting PCL to regenerated cellulose or starch;
- (n) aliphatic/aromatic or aromatic copolyesters optionally grafted with above (a)-(i) products;
- (o) polymers from natural origin such as cellulose, emicellulose, lignin, cellulose ethers and xanthates, regenerate cellulose, pullulan, chitin, chitosan, pectins, proteins, vegetable and animal gelatines, zein, gluten, casein, albumen, natural or modified rubbers, alginates, rosin derivatives.

The aliphatic chains can be grafted by means of any known type of reaction, and generally by:

- (1) transesterification of ester group;
- (2) esterification of hydroxy groups;
- (3) urethanizing hydroxy groups by means of isocyanates;
- (4) epoxidizing hydroxy groups with aliphatic epoxides;
- (5) acetylation of hydroxy groups with aliphatic aldehydes.

The compatible polymers with the cellulose derivatives and starch esters or ethers, polyols soluble in starch, or capable of complexing starch, can be grafted for example with following polyols: modified amylose and its hydrolysis product; polyvinyl alcohol with various hydrolysis degrees, ethylene-vinyl alcohol copolymers, polyols of glycerol, polyglycerol, saccharides, oligosaccharides, trimethylol propane, pentaerythritol.

The number of grafted chains are comprised within the range of from 0.1 to 30 grafted chains per each 100 monomeric units in the polymer chain, preferably from 0.2 to 20, and still more preferably, from 0.3 to 10, grafted chains for each 100 monomeric units.

Besides the compatibilizers of above (A) type which require that polymeric products are modified by grafting lipidic chains, also copolymers of above (B) type can be advantageously used, particularly those obtained from such aliphatic polyesters such as polycaprolactone with various molecular weight and polyethylene succinates, from aliphatic or aromatic diisocyanates or copolymers obtained from C_2 - C_{24} hydroxy acids, or aliphatic or aromatic diisocyanates, or copolymers of above (C) type.

For the preparation of copolymers of above (B) type, preferred diisocyanates are:

- 4,4'-diphenylmethane diisocyanate, hydrogenated 4,4'-diphenylmethane diisocyanate, toluidene diisocyanate, isoforone or hexamethylene-diisocyanate.

Estane (a caprolactone:urethane copolymer traded by Goodrich as "54351 grade") is a representative copolymer of (B) class.

The compositions comprise the starchy component and the cellulose derivatives in ratios by weight comprised within the range from 1:90 to 90:1, preferably from 1:40 to 40:1 and still more preferably of 1.5:5 to 1:1.5.

The compatibilizer agents are present in amounts comprised from 0.1 to 20% by weight, preferably of from 0.5 to 10%.

The plasticiser for cellulose phase and the starchy phase are present in amounts respectively comprised from 5 to 40%, and still more preferably, of from 10 to 30%, by weight.

Compounds which act as plasticizers for both phases, such as, diacetins, can be used.

The total amount of plasticizer is generally comprised from 5 to 40% based on total weight of the composition, preferably from 10 to 30%.

Besides the components indicated above, the composition can also contain synthetic polymers in amount up to about 30% by weight, preferably less than 10%.

Examples of synthetic polymers which can be used are polyvinylalcohol, polyvinyl acetate, thermoplastic polyesters, such as polycaprolactone, copolymers of caprolactone with isocyanates, lactic acid polymers, polyethylene or

polybutylene adipate or sebacate.

The starch which can be used to prepare the compositions according to the present invention generally is a native starch, extracted from various plants, such as maize, potato, wheat, tapioca and cereal starch. Under the term "starch" are also included high amylopectin starches ("waxy" starches), high-amylose starches, chemically and physically modified starches e.g., starches the acid number of which is reduced down to a value comprised within the range from 3 to 6; starches in which the type and concentration of cations associated with phosphate groups are modified; starch ethoxylated, starch acetates, cationic starches, hydrolysed starches, oxidized and crosslinked starches.

Representative cellulose esters comprise cellulose acetates, propionates and/or butyrates, with various degrees of substitution. Cellulose acetate with degree of substitution comprised from 1.5 to 2.5 are preferred.

Example of cellulose and starch ethers are ethyl or propyl ethers.

Cellulose esters or ethers in neat form, mainly the acetate esters, have so high processing temperature as to cause the matrix to undergo severe degradation. They require the use of a plasticizer which can be selected from:

- glycerol esters with aliphatic acids containing up to 6 carbon atoms, in particular diacetin and triacetin;
- esters of citric acid, in particular trimethyl or triethyl citrate, as well as acetyl-triethyl-citrate;
- dialkyl esters of tartaric acid;
- esters of aliphatic acids, lactones and lactides;
- dialkyl esters of aliphatic acids such as those derived from oxalic, glutaric, adipic, sebacic, suberic, azelaic acids, mainly dibutyl adipate and dibutyl sebacate;
- dialkyl esters of aromatic acids in which the alkyl group contains from 1 to 10 carbon atoms, in particular dimethyl phthalate, diethyl phthalate, methoxy and ethoxy ethyl phthalate;
- polyethylene glycol adipate, glutarate or sebacate;
- alkyl and aryl phosphates, in particular triethyl and tricresyl phosphates;
- alkyl ester or fatty acids, such as butyl oleate;
- polymeric plasticizers as the product traded as Paraplex by Rohm and Haas; Admex 719 from Arche Daniels Midland; the Flexol series from Union Carbide;
- non-bleeding plasticizers as: mixed aliphatic-aromatic esters of trimethylol propane and pentaerythritol; alkyl phosphate terminated polyethylene glycols.

In order to obtain the thermoplastic character of the starchy phase, in particular at low humidity contents, polar substances are added, which are capable of forming hydrogen bonds with amylose and amylopectin. Suitable substances for that purpose are polyols with 1-20 repeating hydroxylated units, each containing from 2 to 6 carbon atoms: ethers, thioethers, organic and inorganic esters, acetates and amino derivatives of the above polyols; the reaction products of the polyols with chain extenders; polyol oxidation products containing at least one aldehydic or carboxy group. Plasticizers of this type are disclosed in WO 92/19680 application, the disclosure of which is incorporated herein by reference.

Preferred plasticizers are those which act as plasticizers for both the starchy and the cellulosic phase and the acetins belong to this preferred class.

The starchy phase is normally plasticized directly during the compounding step, in mixture with all the other components. However, also a two step process can be used in which the starchy phase and the cellulosic phase are individually plasticized and/or the starchy phase is plasticized prior to the final compounding step.

Preferred plasticizer comprise: water, glycerol, glycerol ethoxylate, ethylene or propyleneglycol, polyethylene glycol, polypropyleneglycol, 1,2- propanediol, 1,3 propanediol, 1,2-, 1,3-, 1,4- butanediol, 1,5- pentanediol, 1,6-, 1,5-hexanediol, 1, 2, 6-, 1,3,5-, hexanetriol, neopentylglycol, sorbitol acetate, sorbitol diacetate, sorbitol monoethoxylate, sorbitol diethoxylate, trimethylol propane monoethoxylate, mannitol monoacetate, mannitol monoethoxylate, butyl glucoside, glucose monoethoxylate, sodium salt of carboxymethylsorbitol, polyglycerol monoethoxylate.

The preparation of the composition according to the present invention comprises blending the components in a heated extruder or in any device which may secure temperature shear stress conditions sufficient to cause the conversion of the starchy material and the cellulose derivatives into a thermoplastic state and to render the components compatible with each other as regard their rheology, operating at a temperature comprised within the range of from 80 to 210° C in the presence of water and a plasticizer.

The preferred method for preparing the compositions comprises:

- a first step consisting in conveying the components through an extruder with residence times of the order of from 2 to 50 seconds, during which the starchy components and cellulose derivatives are caused to undergo swelling due to the action of the plasticizer and optionally added water, by operating at a temperature comprised within the range from 80 to 180°C;
- a blending step during which the mixture from the preceding step is submitted to shear stress conditions which

correspond to similar viscosity values of the cellulose derivatives and the starchy components:

- optionally a step of venting under controlled pressure conditions or in vacuo in order to obtain a molten mass preferably at a temperature comprised within the range from 130 to 180° C with a water content preferably smaller than 6% such as not to have bubbles formation at atmospheric pressure. e.g., at the extruder outlet, if producing foamed products is not desired. This condition is satisfied when it is desired to obtain not foamable products.

In the case of foamable products, the water content in the blend may be as high as 20%, preferably up to 18%.

The resulting molten mass can be then directly extruded into pellets from which articles are then fabricated by means of the conventional processes.

The following examples are supplied in order to illustrate the invention without limiting it.

EXAMPLES

Examples 1-8 are comparison examples; examples 9-22 are according to the invention.

(A) Blending

The compositions were prepared by using a twin-screw APV extruder Mod. 2030 of 30mm of diameter, with L:D = 25. The temperature profile of the 16 temperature controlled zones was as follows:

$$60^{\circ}\text{C} \times 1 - 100^{\circ}\text{C} \times 1 - 180^{\circ}\text{C} \times 14$$

The screw revolution speed was 120 rpm.

(B) Injection moulding

The pellets obtained from the extruder were fed to a Sandretto injection press Series 60 in order to obtain dumbbell-shaped specimens. The test results are reported in following table 1

Table 1

	1	2	3	4	5	6	
Aceplast LS	75	80	75	44	4-	64	
CAB	--	--	--	--	44	--	
Acetyl triethyl citrate	--	--	25	--	--	--	
Diacetin	25	--	--	--	--	--	
Epoxidized soy bean oil	--	--	--	16	16	--	
Caprolactone	--	20	--	--	--	16	
Mat-1	--	--	--	--	--	20	
Mat-2	--	--	--	--	--	--	
Maize Starch	--	--	--	32	32	--	
Acetylated starch with DS 1.3	--	--	--	--	--	--	
Acetylated starch with DS 2.0	--	--	--	--	--	--	
Sorbitene (ethoxilated sorbitol)	--	--	--	7.8	78.8	--	8
Erucamide	--	--	--	0.2	02.2	--	2
FOOTNOTES	a	a	a	b	a,c	a	b

Table 1 (continued)

	12	13	14	15	16	17	18	19	20	21	22
Aceplast LS	44	44	44	44	44	44	44	44	38	38	45
Diacetin	16	16	16	16	16	16	16	16	14	14	--
Maize Starch	24	27	27	27	27	27	27	27	25	30	29
Acetylated starch with DS 1.3	--	--	--	--	--	--	--	--	5	--	16.5
Acetylated starch with DS 2.0	--	--	--	--	--	--	--	--	--	--	--
Sorbilene	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	8.3
Eucarimide	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
SAC DS 1.3/laurate 0.3	5	--	--	--	--	--	--	--	--	--	--
SAC DS 1.3/laurate 0.9	--	5	--	--	--	--	--	--	--	--	--
SAC DS 1.3/laurate 2.2	--	--	5	--	--	--	--	--	--	--	--
SAC DS 1.3/laurate 4.6	--	--	--	5	--	--	--	--	--	--	--
SAC DS 1.3/laurate 9.1	--	--	--	--	5	--	--	--	--	--	--
SAC DS 2.1/laurate 3.6	--	--	--	--	--	5	--	--	--	--	--
SAC DS 2.1/laurate 3.2	--	--	--	--	--	--	5	--	--	--	--
SAC DS 2.1/oleate 2.8	--	--	--	--	--	--	--	5	--	--	--
Estane	--	--	--	--	--	--	--	--	10	--	--
AC/EVOH	--	--	--	--	--	--	--	--	--	10	--
Sorbitol trioleate ethoxylate	--	--	--	--	--	--	--	--	--	--	1
FOOTNOTES	c	d	d	a, d	c	d	a, d	a, d	d	d	d

LEGEND

1) Aceplast LS is a cellulose acetate with substitution degree 2.5, traded by Società acetati S.p.A. of Verbania, Italy.

2) CAB is a cellulose acetate/butyrate traded by Eastman chemicals under their trademark CAB 831-20.

3) The composition of both MAT-1 and MAT-2 products, obtained according to as reported in Italian patent application IT 67413/A89 is as follows:

	MAT-1	MAT-2
Starch	39	36
EAA-20	3	--
EVOH	36	22
PVOH	--	22
Glycerol	16.7	15.2
Urea	5	4.5
Armid-E	0.3	0.3

4) Acetilated starch with DS=1.3 is manufactured by national Starch and is referred to as "78-0403 GDS-1233". Acetilated starch with DS=2 is a laboratory sample obtained in pyridine with acetic anhydride.

5) The compatibilizer agents reported in the Table were obtained from starch acetate (SAc) with SD 1.3 and 2.1 and cellulose acetate (CAc) with SD 2.1

The substitution percent rate is indicated as a suffix to the designation of the grafted acyl radical: it is expressed as the number of the resulting grafted radicals per each 100 monomeric units of substrate.

The fatty acid grafting reaction was carried out using lauric and oleic acid chlorides in dimethyl acetamide.

After neutralisation with pyridine, the compatibilizer agents deriving from starch acetate and cellulose acetate were precipitated with ethyl ether and water respectively.

6) Estane is a caprolactone/urethane copolymer traded by Goodrich as grade 54351.

7) AC/EVOH is a copolymer of cellulose acetate grafted with 10% of a copolymer of ethylene with vinyl alcohol. Cellulose acetate with SD of 2.9 is plastified in a monoscrew extruder OMC with 20mm diameter, with 27% by weight of triacetin. The extruder was operated at 195° and 140 rpm. The pellets were added with 1.3 w% of ex-amethylendiamine diisocyanate and extruded again at 170° C and 140 rpm. The pellets thus obtained were added with 10w% of EVOH A4412 of Nippon Goshei and extruded at 180°C and 6 rpm.

Footnotes to table 1

(A): the material was tested for biodegradability (see data reported in table 2).

(b): the dumbbell specimen, obtained by injection moulding operating according to above "B" condition, undergoes severe delamination;

(c): the dumbbell specimen, obtained by injection moulding according to above "B" operating condition, tends to delaminate;

(d): the morphology of the surface of the dumbbell specimen appears to be homogeneous, with no scales apparent (see photographs).

Biodegradability of the compositions disclosed in the Examples

The biodegradability of the materials was tested by recording the weight loss of specimens enclosed inside polypropylene nets (with 1mm mesh) embedded inside a substrate of an aged composite with 55% of moisture and heated at 50% inside an incubator. A plurality of specimen, i.e., one specimen each net, are charged, so as to able to follow the course of degradation over time. Per each specimen, 50 g of composite is used. The initial weight of the specimen is recovered, is washed in water and the with ultrasounds at 20°C and 55% RH, and is finally weighed.

Table 2

Weight loss undergone by specimens after

	15 days	60 days	150 days
Example 1	18.6	23.1	26.3
Example 2	15.8	19.6	24.8
Example 3	18.8	24.1	25.8
Example 5	29.8	39.1	51.7
Example 6	32.1	84.7	91.2*
Example 7	25.2	86.3	93.2*
Example 9	30.1	89.8	96.9*
Example 10	27.1	85.9	97.1*
Example 15	29.8	86.7	98.0*
Example 18	30.4	88.8	97.4*
Example 19	29.2	91.1	97.5*

(*) The found residue is black and its appearance is absolutely different from the appearance of the starting polymer. This is evidently material turned into humic type derivatives. Therefore, the indicated values can be regarded as being equivalent to 100% degradation.

Surface morphology of dumbbell specimens

The inspection of the dumbbell specimens for their surface morphology was carried out by optical microscopy (Wild Macroscope M-420) and SEM electronic microscopy (Stereoscan 260 ex Cambridge Instruments). The optical microphotographs are in reflected light, with 45 x magnification. For SEM microphotographs, the magnification rate is reported on the images.

As one will observe from the picture, the addition of the compatibilizer according to the present invention causes a sharp increase in dumbbell specimen surface quality (in the most meaningful cases, the microphotographs obtained from both techniques are reported).

Following pictures No 1 and 2 relate to Example 20 and 21 respectively.

Claims

1. Biodegradable thermoplastic composition comprising starch or a starch ester or ether, a cellulose ester or ether, a plasticizer for the starchy phase, a plasticizer for the cellulose ester or ether phase, or a plasticizer for both phases, and a compatibilizing agent for the starchy phase and the cellulose ester or ether phase selected from:
 - (A) polymers or copolymers compatible with the cellulose esters or ethers, and/or with starch or starch esters or ethers, grafted with aliphatic or polyhydroxylated chains containing from 4 to 40 carbon atoms;
 - (B) copolymers obtained from hydroxy acids or diamines with 2-24 carbon atoms aliphatic or aromatic diisocyanates or epoxy compounds and anhydrides; copolymers obtained from aliphatic polyesters, polyamides or polyureas and aliphatic or aromatic diisocyanates; copolymers obtained from, aliphatic and aromatic diisocyanates and polyalkylene glycols;
 - (C) copolymers obtained from polymers compatible with cellulose esters or ethers and/or starch or starch esters and ether, by grafting starch soluble polyols or structures capable of complexing starch.
 - (D) polymers capable of complexing starch.
 - (E) starch compatible polyols selected from the monomers and polymer with molecular weight lower than 10.000;
2. Compositions according to claim 1, in which the ratio of starchy component to cellulose derivative, is comprised within the range from 1: 90 or to 90:1 by weight, and the compatibilizer agent is used in amounts from 1 to 20% by weight based on the total amount of starchy components and the cellulose derivatives.
3. Compositions according to claim 1 and 2, in which the compatibilizer is selected from polymers or copolymers as the class (A) above and in which the grafting degree is comprised within the range from 0.1 to 30 grafted aliphatic chains per each 100 monomeric units in the polymer chain.
4. Composition according to claim 4, in which the grafted chains present in compatibilizer derive from animal or vegetable fats.
5. Composition according to claim 4, in which the grafted chains derive from oleic, lauric, myristic, palmitic, stearic, erucic, linoleic or ricinoleic acid.
6. Compositions according to claim 1 or 2, in which the compatibilizer agent is a block copolymer obtained from polycaprolactone and aliphatic or aromatic diisocyanate.
7. Compositions according to claim 6, in which the copolymer is obtained from polycaprolactone and diisocyanate selected from 4,4'-diphenylmethane diisocyanate, toluidene diisocyanate and hexamethylene diisocyanate.
8. Compositions according to claims 1 or 2, in which the (C) compatibilizer is a copolymer obtained by grafting a polyol selected from polyvinyl alcohol, ethylene-vinyl alcohol copolymers, glycerol, polyglycerol, saccharides, trimethylol propane, pentaerythritol.
9. Compositions according to claims 1, 2, 3, 4, 5, 6, 7, or 8, in which the cellulose ester is cellulose acetate with a substitution degree from 1.2 to 2.5.
10. Compositions according to claims 1, 2, 3, 4, 5, 6, 7, or 8, in which the plasticizer are present in amounts comprised

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within from 5 to 40% by weight, on the total composition weight.

11. Compositions according to claims 1, 2, 3, 4, 5, 6, 7 or 8, in which the plasticiser for starchy phase and cellulose ester or ether is diacetin.

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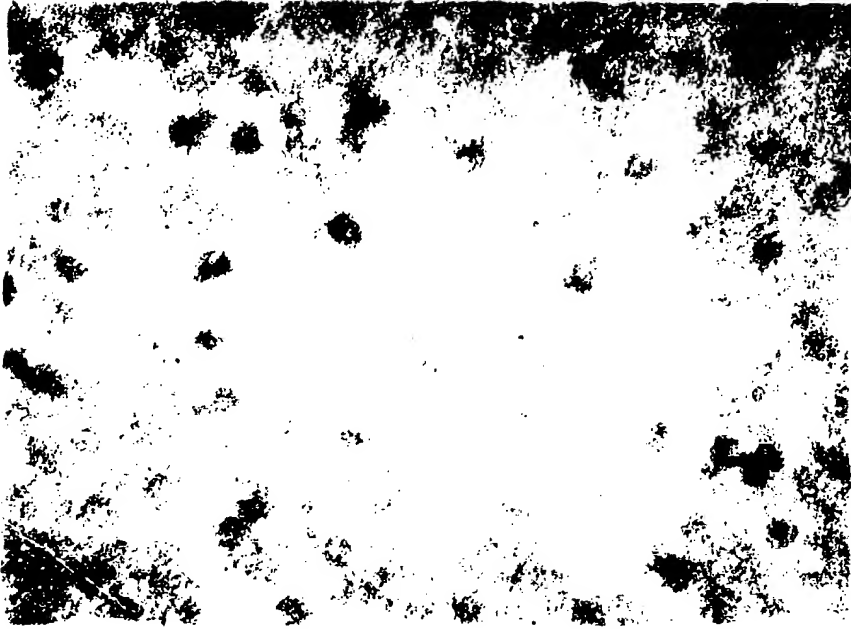
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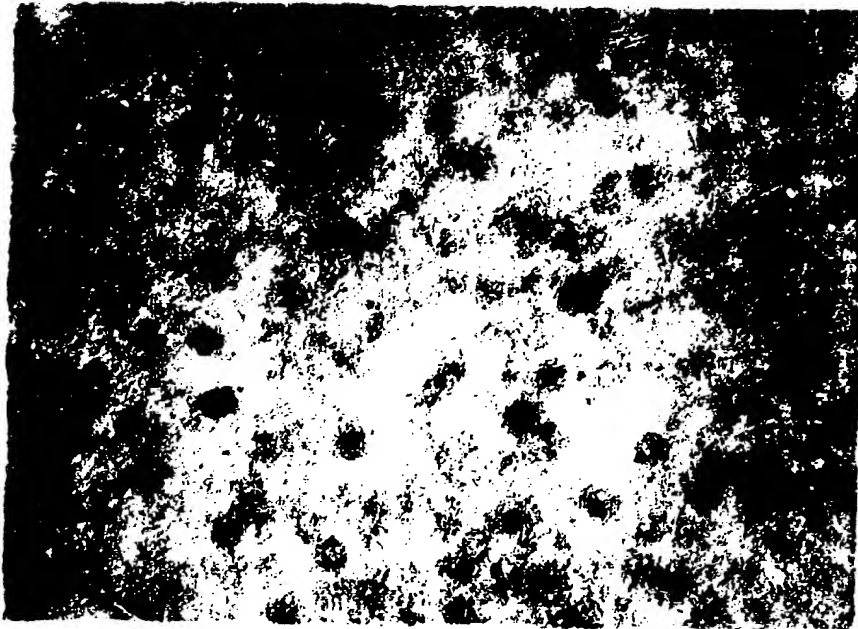
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Picture 2



Picture 1



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 10 0035

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	EP-A-0 409 781 (WARNER-LAMBERT COMPANY) * page 5, line 31 - line 34 * * page 7, line 23 - line 47 * ---	1-11	C08L1/12 C08L3/00
Y	US-A-5 288 318 (MAYER ET AL.) * column 7, line 1 - line 56 * ---	1-11	
Y	DATABASE WPI Week 8114 Derwent Publications Ltd., London, GB; AN 243880 XP002002938 & JP-A-56 014 544 (NIPPON SYNTH CHEM IND) , 12 February 1981 * abstract * ---	1-9	
D,Y	EP-A-0 542 155 (TOMKA IVAN) * claim 8 * ---	1-9	
D,A	WO-A-92 14782 (NOVAMONT) & EP-A-0 575 349 ---		TECHNICAL FIELDS SEARCHED (Int.Cl.6)
E	EP-A-0 696 611 (NOVAMONT) 14 February 1996 * page 3, line 16 - line 17 * ---	1	C08L
P,X	DATABASE WPI Week 9524 Derwent Publications Ltd., London, GB; AN 183084 XP002002939 & JP-A-07 102 114 (TEIJIN LTD) , 18 April 1995 * abstract * -----	1-9	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13 May 1996	Examiner Lensen, H
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone V : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application f : document cited for other reasons ----- & : member of the same patent family, corresponding document</p>			

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